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Dissolution methods for strontium isotope stratigraphy: whole rock analysis

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Abstract

The preparation of samples for strontium isotope stratigraphy (SIS) by whole rock dissolution results in contributions of Sr from contaminant phases as well as from the target carbonate phase. Here we highlight and quantify the errors in $^{87}Sr/^{86}Sr$ values that might result when calcium carbonate is dissolved using an inappropriate method. We report the variation in $^{87}Sr/^{86}Sr$ value of Sr released from four samples of differing calcite content and degrees of cementation, when subject to different methods of dissolution. We show that errors of up to ± 0.000076 in $^{87}Sr/^{86}Sr$, which correspond to errors of ± 3.68 Ma in age, can be avoided by careful preleaching of the samples. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Strontium isotope stratigraphy; Whole rock; Leaching

1. Introduction

Strontium isotope stratigraphy (SIS) is finding widespread use for the dating and correlation of sediments (Elderfield, 1986; Veizer, 1989; McArthur, 1994; Howarth and McArthur, 1997). When using SIS, it is crucial that Sr is isolated from the target mineral without being contaminated with Sr from extraneous phases. This problem is an acute one when whole rock analysis is used (e.g., DePaolo et al., 1983; DePaolo and Ingram, 1985; Hein et al., 1993; McArthur et al., 1994; Meisel et al., 1995; Eisenberg et al., 1996; Whitford et al., 1996, Denison et al., 1997; amongst others). Isolation of target Sr has been undertaken using sample dissolution methods ranging from an acid preleach prior to partial dissolution in weak acid (McArthur et al., 1993a,b), to a total dissolution in mixed strong acids (Hein et al., 1993). Some workers are aware of the dangers posed by acid attack on nontarget minerals, and employ preleaches in order to minimise contamination (e.g., DePaolo et al., 1983; Ohde and Elderfield, 1992; McArthur et al., 1993a; Montanez et al., 1996). The degree of contamination caused by failure to use preleaches remains unquantified. Furthermore, little attention has been given to contamination arising from progressively greater attack on insoluble residues as target carbonate dissolves. This leaves a

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potential source of contaminant that can be more serious than previously supposed.

2. Samples

The samples investigated comprised two chalks, a marl, and an indurated limestone. All samples were ground by hand using an agate pestle and mortar.

Sample L: a weakly cemented, middle Campanian, friable nannofossil chalk from Lagerdorf, Germany, that contains 96% $CaCO_3$ and 544 ppm Sr (sample 50 of McArthur et al., 1993a). An $^{87}Sr/^{86}Sr$ value of 0.707586 ± 10 was reported by these authors. Comparisons with samples at the same stratigraphic level in the English chalk (McArthur et al., 1993b) and the US western interior (McArthur et al., 1994) suggest that this $^{87}Sr/^{86}Sr$ accurately reflects the marine $^{87}Sr/^{86}Sr$ at that time.

Sample T: a lower Santonian chalk from a depth of 351.4 m in a chalk borehole at Trunch, Norfolk, UK. This chalk sample was slightly harder and more cemented than Sample L and contained 98% $CaCO_3$ and 715 ppm Sr (McArthur et al., 1993b). Comparisons with samples at a similar stratigraphic level within the borehole (ibid.) and in the US western interior (McArthur et al., 1994) suggest that its $^{87}Sr/^{86}Sr$ should be 0.707450 ± 20.

Sample E: an impure, moderately cemented, nannofossil chalk from 5 m below the Cenomanian–Turonian boundary in the English Lower Chalk near Dover, East Kent, UK. This sample contained 78% $CaCO_3$ and 550 ppm Sr. Comparisons with samples at a similar stratigraphic level within the English

Table 1
$^{87}Sr/^{86}Sr$ and percentage of carbonate dissolved for each dissolution method. Note that for some of the data, an averaged value (*) was plotted on Fig. 1 for clarity

% Carbonate dissolved	$^{87}Sr/^{86}Sr$	% Carbonate dissolved	$^{87}Sr/^{86}Sr$
Lagerdorf		*Trunch*	
Water wash	0.707767	Water wash	0.708434
Ammonium acetate	0.707644	Ammonium acetate	
5.9	0.707625	7.4	0.707886
17.4	0.707606	19.6	0.707536
30.6	0.707601	33.0	0.707478
42.9	0.707603	45.4	0.707484
53.7	0.707567	56.7	0.707483
75.0	0.707571	75.9	0.707515
90.4	0.707597	90.8	0.707487
99.3	0.707607*	94.9	0.707668
99.6	0.708362*	100.0	0.707804
100.0	0.709887		
East Kent		*Gubbio*	
Water wash	0.707764	Water wash	0.707496
Ammonium acetate	0.707516	Ammonium acetate	0.707515
6.9	0.707588	9.1	0.707478
20.1	0.707492	22.4	0.707403
38.2	0.707461	40.5	0.707388
54.1	0.707430	55.0	0.707356
65.8	0.707429	68.6	0.707370
76.3	0.707438	78.5	0.707401
90.5	0.707443	88.9	0.707445
98.1	0.707458*	95.4	0.707412*
99.2	0.707696*	96.2	0.707869*
99.4	0.708618*	96.6	0.708297*
99.6	0.708992*	100.0	0.708089
100.0	0.717831		

Chalk in Norfolk (McArthur et al., 1993b) and in the US western interior (McArthur et al., 1994) suggest that its $^{87}Sr/^{86}Sr$ should be 0.70739 ± 2.

Sample G: an impure, hard, lithified, pelagic chalk from 1.5 m above the Cenomanian–Turonian boundary in the Contessa Valley, Gubbio, Italy. This sample contained 74% $CaCO_3$ and 387 ppm Sr. Comparison with the data near this stratigraphic level in other sequences (McArthur et al., 1993b; 1994) suggests that its $^{87}Sr/^{86}Sr$ value should be 0.707380 ± 20.

3. Methods

3.1. Sr soluble in water and 1 M ammonium acetate

To assess the amount of Sr, and the $^{87}Sr/^{86}Sr$ released by water washing and washing with 1 M ammonium acetate, 4 g of sample were leached in 10 ml of each reagent for 24 h and the leachate separated by double centrifugation and pipette for analysis of $^{87}Sr/^{86}Sr$ (see Table 1 for results).

3.2. Sr soluble in dilute weak acid

To assess the amount and $^{87}Sr/^{86}Sr$ of Sr soluble in sequential leaches in a dilute weak acid (acetic acid), approximately 100 mg of accurately weighed samples were placed into centrifuge tubes and covered with 2 ml of ultrapure water. To each sample accurately known sequential volumes of the order of tens of microlitres of 20% acetic acid were added, and the sample was ultrasonically agitated until reaction ceased. The supernatant was separated by pipette after double centrifugation and was analysed for Sr concentration and $^{87}Sr/^{86}Sr$ (see below). The acid volumes were designed to dissolve the carbonate in the sample in accurately known steps of around 10%.

3.3. Sr soluble in mixed strong acids

After sufficient acetic acid had been added to dissolve 100% of the carbonate, the remainder of the sample was then treated with strong acid (6M HCl + 6M HNO_3) for 24 h at room temperature and the supernatant separated as before for measurement. This process yields an approximate measure of the $^{87}Sr/^{86}Sr$ of trace insoluble impurities that can contribute Sr from a residuum if overly aggressive dissolution methods are used.

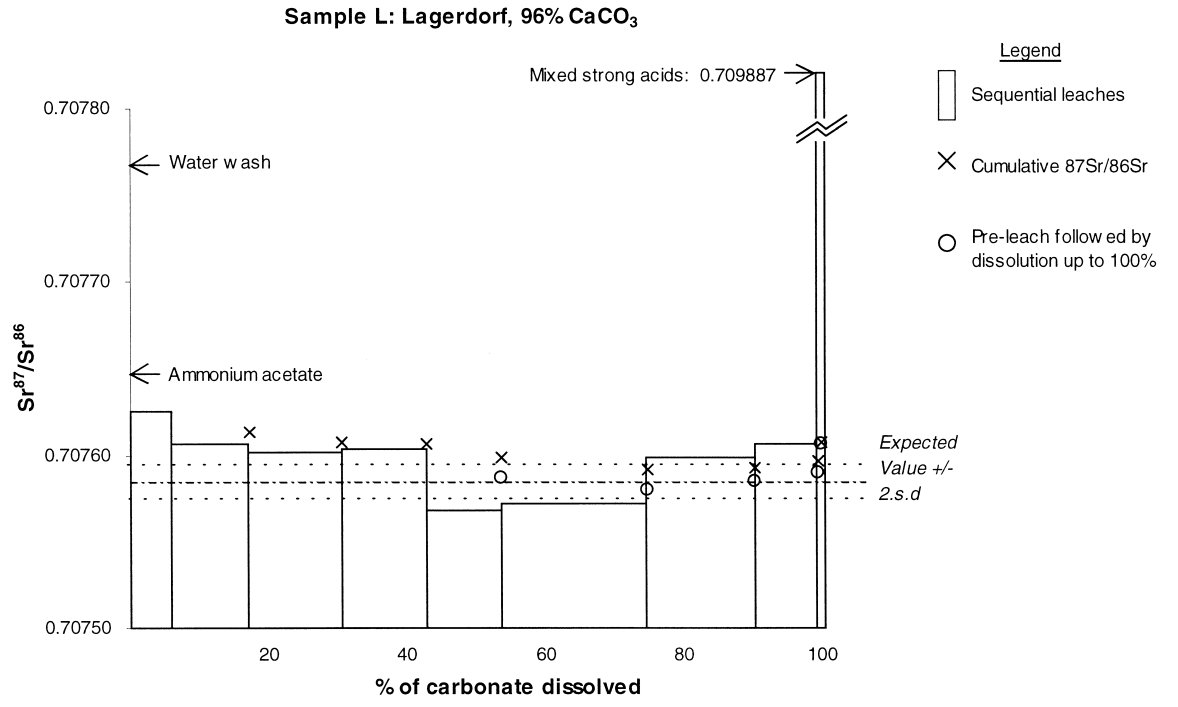
In all cases, $^{87}Sr/^{86}Sr$ and Sr concentration by isotope dilution were measured with a VG 354 multicollector thermal ionisation mass spectrometer using multidynamic procedures as described in Thirlwall (1991). Blank Sr quantities were measured for all the steps and procedures used here and found to be an insignificant influence on the results.

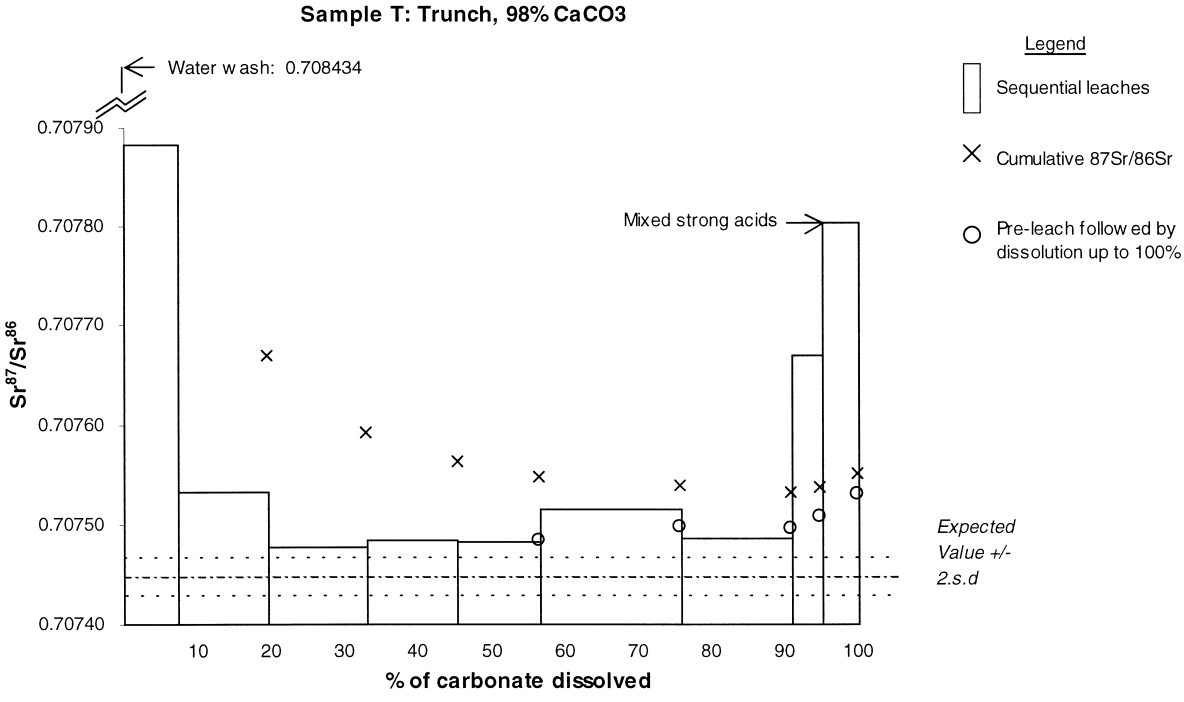
4. Results

The results are presented in Table 1 and Fig. 1. Water-soluble Sr constitutes 0.23% (Sample E) to 1.3% (Sample T) of the total Sr in the samples. In all cases, water soluble Sr has an $^{87}Sr/^{86}Sr$ value that is higher than that in the bulk of the sample; this difference ranges from 0.000096 for sample G to 0.000963 for sample T. This Sr is probably derived from the dissolution of evaporated groundwater salts and from ion-exchange sites. The high proportion of water soluble Sr in sample T might arise from dissolution of trace celestite ($SrSO_4$), which is known to be present in this core at the depth from which this sample was taken (Bath and Edmunds, 1981; McArthur et al., 1993b).

Leaching with 1 M ammonium acetate yields a solution with an $^{87}Sr/^{86}Sr$ value higher than that for the bulk of the sample but generally lower than that of the water leach, probably because ammonium acetate not only dissolves groundwater salts and displaces contaminant Sr on ion-exchange sites, but also weakly complexes Ca and so dissolves calcite. The Sr obtained at this step therefore represents a mixture of Sr from contaminant sources and that from calcite.

Fig. 1 shows that the $^{87}Sr/^{86}Sr$ of the first and last acetic acid leaches (up to ~30% dissolved, and ~90–100% dissolved) are higher than those of the intermediate leaches (30–90% dissolved) for each sample. The initial leaches incorporate water-soluble Sr from ion-exchange sites. The increasing $^{87}Sr/^{86}Sr$ values from ~90–100% dissolved, culminating in the very high values obtained by treatment with


Sample L: Lagerdorf, 96% CaCO3
Mixed strong acids: 0.709887
Legend
Sequential leaches
Cumulative 87Sr/86Sr
Pre-leach followed by dissolution up to 100%
0.70780
Water wash
0.70770
Ammonium acetate
Sr87/Sr86
0.70760
Expected Value +/- 2.s.d
0.70750
20
40
60
80
100
% of carbonate dissolved


Sample T: Trunch, 98% CaCO3
Water wash: 0.708434
Legend
Sequential leaches
Cumulative 87Sr/86Sr
Pre-leach followed by dissolution up to 100%
0.70790
0.70780
Mixed strong acids
0.70770
Sr87/Sr86
0.70760
0.70750
Expected Value +/- 2.s.d
0.70740
10
20
30
40
50
60
70
80
90
100
% of carbonate dissolved

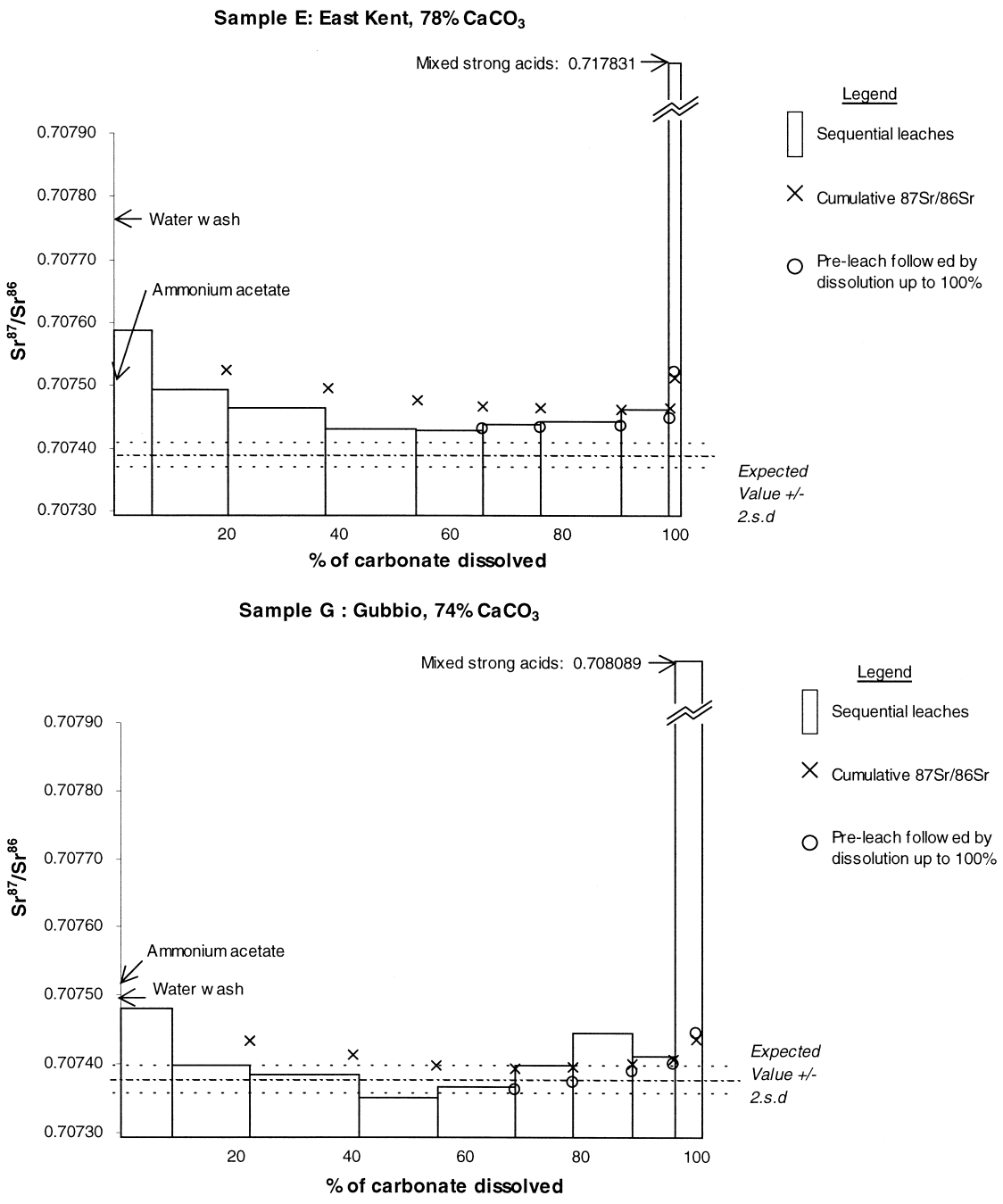


Figure 1. The $^{87}Sr/^{86}Sr$ of sequential leaches in 20% acetic acid is plotted against the percentage of carbonate dissolved. Arrows show $^{87}Sr/^{86}Sr$ values for the water wash, ammonium acetate, and strong acid treatments. 'Cumulative $^{87}Sr/^{86}Sr$' (crosses) shows the $^{87}Sr/^{86}Sr$ trend calculated by applying the two end-member mixing model to the successive leaches as described in the text. This provides a simulation of how the $^{87}Sr/^{86}Sr$ evolves throughout bulk dissolution. Circles show the results obtained by preleaching prior to dissolution in acetic acid. The data from the first three leaches were discarded, and the cumulative $^{87}Sr/^{86}Sr$ trend up to 100% dissolved was predicted using the model.

mixed strong acids, is thought to be the result of acid attack on a noncarbonate residuum, which becomes relatively increased in abundance as carbonate dissolves. Aluminosilicates are thought to be the source of this residual Sr as this feature is most pronounced in the marl sample (sample E).

5. Modelling of $^{87}Sr/^{86}Sr$ trends during dissolution

The evolution of $^{87}Sr/^{86}Sr$ during an acetic-acid bulk dissolution was modelled using a two end-member mixing model adapted from Faure (1986). To take sample T as an example, the model predicts the $^{87}Sr/^{86}Sr$ after dissolution of $\sim$20% of carbonate by mixing the two end members of 0.707886 ($\sim$0–10% leach) and 0.707536 ($\sim$10–20% leach). The next value in the trend is obtained by mixing the result of the previous calculation with the $^{87}Sr/^{86}Sr$ of the next leach (0.707478, $\sim$20–35% dissolved).

Fig. 1 shows the variation in $^{87}Sr/^{86}Sr$ obtained by the different methods of bulk dissolution ('Cumulative $^{87}Sr/^{86}Sr$') and preleaching followed by 100% dissolution. This shows that were the Sr removed from the samples by the first and final leaches not discarded prior to isolation of Sr for analysis of $^{87}Sr/^{86}Sr$, it would have increased the final ratios by 0.000023 for L, 0.000056 for T, 0.000076 for E, and 0.000046 for G. These discrepancies are small but significant with regard to SIS where analytical precision may be $\pm$0.000019 (2.s.d.) for routine single analyses (Thirlwall, 1991) or as low as $\pm$0.000004 (2.s.e.) for replicate determinations (Crame et al., 1999). Using the standard seawater $^{87}Sr/^{86}Sr$ curve and look-up table of Howarth and McArthur (1997) the discrepancies translate to systematic uncertainties in age of 1.24 Ma for sample L, 3.65 Ma for T, 3.68 Ma for E, and 1.71 Ma for G (the average uncertainty in age propagated by the analytical precision is 0.86 Ma).

The final strong acid leach in each case is significantly greater than the bulk $^{87}Sr/^{86}Sr$ and increases the preleached trend at $>$90% carbonate dissolved. This shows the dangers of allowing even trace amounts of noncarbonate material to contribute Sr to dissolution steps.

6. Conclusions

Sr from nontarget phases may contaminate the original $^{87}Sr/^{86}Sr$ of a sample by substantial amounts and must be avoided when measuring $^{87}Sr/^{86}Sr$ for SIS. Acidic preleaches in acetic acid seem able to effectively remove much of the contamination from pure and impure limestones and chalks. Precleaning with water and ammonium acetate does not remove all contaminant Sr. An acidic preleach dissolving up to 40% of the sample will remove much of the contaminant Sr on exchangeable sites and will dissolve a good part of the secondary carbonate overgrowths that might contain secondary contaminant Sr. A further 30% of the sample should then be dissolved in dilute acetic acid and separated for analysis. At least 10% of the carbonate should be left undissolved in order to ensure no contribution from matrix incorporated impurities which can be attacked by acid at low concentrations of carbonate. This will also ensure that the final solution is not acidic during the centrifugation and separation of Sr; if all the carbonate were to dissolve, then the noncarbonate residuum would suffer continued acid attack during this step and contaminant Sr might be leached from it as a result.

Note that for samples E and T, even the use of careful leaching does not yield the expected results, with the samples giving $^{87}Sr/^{86}Sr$ values, around 0.000010 to 0.000020, too high. For these samples, the difference is thought to be the expression of an unknown diagenetic factor, which has affected the stratigraphic sections. This stresses the importance of the application of careful sample selection procedures, as well as suitable preparation techniques for the $^{87}Sr/^{86}Sr$ analyses used in SIS.

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